

Distribution and Weathering of Macondo Oil Stranded on Shorelines in 2010 based on Chemical Fingerprinting

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Abstract

Stranded oil – tarballs, patties, mats, emulsions, oiled vegetation and debris (n=1333) – collected from supra- and inter-tidal portions of shorelines in Louisiana, Alabama, Mississippi, and Florida between May 24 and November 14, 2010, were chemically analyzed in order to (1) confirm the presence of Macondo oil via chemical fingerprinting and (2) assess their range in composition due to weathering. Results provide a basis for evaluating exposure in the region's beach and marsh ecosystems in the months following the spill and also provide a baseline for future studies.

With respect to extent of stranded Macondo oil in 2010, the following conclusions were reached:

- Fingerprinting revealed 1219 samples (94.1% of those containing sufficient oil for fingerprinting) were comprised of or contained Macondo oil. These spanned at least ~500 miles from western Terrebonne Bay, Louisiana to western Apalachicola Bay, Florida (Fig. 4). The full eastern and western extents are not likely represented by the samples collected, which according to BP reportedly extended as far west as Galveston Bay (Fig. 2).
- Fingerprinting revealed stranded Macondo oil at 190 shoreline locations where SCAT had revealed “*no oil observed*” (Fig. 5), suggesting SCAT did not fully represent the extent of shoreline oiling.

With respect to weathering of stranded Macondo oil in 2010, the following conclusions were reached:

- The stranded Macondo oils studied had lost between 25% and 80% (avg. $55 \pm 6\%$) of the total C_{5+} mass, which exceeded that of previously studied floating Macondo oils (avg. $38 \pm 9\%$; range 15 to 52%). Thus, on average, ~17% additional C_{5+} mass loss occurred during the oil's transport to and/or after becoming stranded on shorelines.
- No relationship existed between the C_{5+} mass loss and sample date (mid-May to mid-November) or distance from the wellhead (50 to 200 miles; Fig. 6) indicating stranded oil degree of weathering cannot be reliably predicted by collection date or location.
- Additional mass loss was mostly due to continued evaporation and dissolution wherein even the least weathered stranded oil studied had lost essentially all mass below $n-C_{15}$, including BTEX, naphthalene, and methylnaphthalenes. In addition, and unlike the floating oils, at least some stranded oils had additional mass loss due to the on-set of biodegradation.
- The concentration of $TPAH_{50}$ in stranded Macondo oil (avg: $1705 \pm 746 \mu\text{g/g}$; range: 333 to 8254 $\mu\text{g/g}$) was lower than in floating (avg: $6640 \pm 4140 \mu\text{g/g}$; range: 1010 to 13,700 $\mu\text{g/g}$) and fresh Macondo oil (13,300 $\mu\text{g/g}$). [Note the “freshest” floating oil was enriched in PAH compared to fresh oil due to weathering of non-PAHs.]



- On average, the floating oils had lost $68 \pm 24\%$ (range: 11 to 95%) of TPAH₅₀, and the stranded oils had lost $94 \pm 3.1\%$ (range: 67 to 99%) of TPAH₅₀ compared to fresh Macondo oil. Thus, on average, ~26% additional loss of TPAH₅₀ occurred during the oil's transport to and/or after becoming stranded on shorelines.
- The percent depletions of individual PAH analytes decreased with increasing ring number and degree of alkylation for homologue groups between decalins and fluoranthrenes/pyrenes (Fig. 9) due to the combined effects of evaporation, dissolution, and/or biodegradation.
- In contrast, the highest molecular weight PAH homologues studied, naphthobenzothiophenes and benz(a)anthracenes/chrysenes, exhibited greater depletions with increasing degree of alkylation (Fig. 9). These depletions, as well as those for triaromatic steroid (TAS) biomarkers (Fig. 10), are attributable to photo-oxidation, the effects of which had progressed beyond those observed in floating Macondo oils.
- Recognizing that photo-oxidation has affected the stranded Macondo oils samples is consistent with other studies showing increased concentrations of oxy-hydrocarbons in stranded Macondo oil (Aeppli et al., 2012) and is notable given the greater toxicity typically associated with photo-oxidized oils.
- Traces of di(propyleneglycol)-n-butyl ethers (DPnBs) were detected in three of the stranded oils, suggesting "residual" Corexit 9500 dispersant may have been transported to shore in some coalesced oil slicks.

Introduction

The environmental fate of crude oil released (between April 20 and July 15, 2010) from the failed Macondo well following the explosion of the *Deepwater Horizon* drill rig varied. Some fraction of the crude oil released remained within the deep ocean, e.g., a dissolved phase and physically or chemically-dispersed, neutrally buoyant droplets (< 40 μ m) were transported laterally at depths of ~1000 to 1300 meters (e.g., Camilli et al. 2010; Hazen et al., 2010; Atlas et al., 2011; Ryerson et al., 2012; Payne and Driskell 2015). However, sufficient buoyancy forces caused another fraction to be transported (roughly) vertically ~1500 meters through the water column to the sea surface. The oil that reached the sea surface formed multiple floating surface slicks, mousses, and sheens.

An earlier report had described the chemical composition and range in weathering observed among 62 floating surface slicks, mousses, and sheens collected from the northern Gulf of Mexico in the spring and summer of 2010 (Stout, 2015a). This study had shown that these floating Macondo oils had lost between 15% and 52% of their C₅+ mass due to weathering (avg. $38 \pm 9\%$). Mass loss was mostly due to evaporation although some additional mass loss due to aqueous dissolution and photo-oxidation was also evident. Mass loss due to microbial biodegradation was not yet evident among the floating oils studied.

Spread by wind and currents, some fraction of floating Macondo oil became "stranded" on shorelines across the northern Gulf of Mexico, arriving over the course of several months. The first oil reportedly reached shorelines in Louisiana on approximately May 15, 2010 and about two weeks later Mississippi, Alabama, and Florida (OSAT, 2011). It produced a highly visible and publicized impact on hundreds of miles of the region's



beaches and (mostly salt) marshes during the spring and summer of 2010 (OSAT 2011; Michel et al. 2013; Mendelssohn et al. 2012).¹

This stranded oil was observed in a variety of visibly-obvious forms including discrete tarballs (<10 cm), patties (10-50 cm), and oil mats (>50 cm). These sometimes occurred as “pure” viscous emulsions of oil but more often were mixtures of sand bound by lesser amounts of oil, i.e., oil-mineral aggregates. Also observed along shorelines were oily coatings on rocks, vegetation, shell hash, and wildlife (Fig. 1). Less visibly-obvious impacts of stranded oil on shorelines included oil adsorbed by dark-colored organic-rich sediments, oil that sunk in sub-tidal areas following its adsorption by suspended particulate matter (SPM, mostly sand), or oil that had become buried on beaches (OSAT 2011; Wang et al., 2013).

All forms of stranded Macondo oil had undoubtedly experienced further chemical changes compared to the floating Macondo oils due to progression in the weathering processes (dissolution, evaporation, biodegradation and/or photo-oxidation) during its transport or after arriving at shorelines. Determining alterations in chemical composition and the ranges of weathering of the stranded Macondo oil is important for understanding its ecological and toxic effects in the region’s beach and marsh ecosystems in the months following the spill.

In this study, the results of chemical analyses on 1333 stranded oils² collected from the supra-tidal (above high tide) and inter-tidal (between high and low tide) zones in shorelines in Louisiana, Alabama, Mississippi, and Florida between May 24 and November 14, 2010 are summarized. (A separate report reviews submerged oil from sub-tidal zones; Stout and Emsbo-Mattingly, 2015.) The objectives are to:

- (1) establish through chemical fingerprinting the spatial extent of visibly-obvious forms of stranded Macondo oils on shorelines in Louisiana, Mississippi, Alabama, and Florida.
- (2) establish the range in chemical compositions (weathering) among stranded Macondo oil between ~1 and 7 months from the start of the *Deepwater Horizon* oil spill.

These objectives collectively provide important bases for understanding the exposure (spatial extent and toxicity) of the natural resources visibly impacted by Macondo oil in nearshore environments in 2010.

All of the data summarized herein were: (1) determined using the analytical methods defined in the Analytical Quality Assurance Plan (NOAA 2014) for the NRDA and (2) measured by a single laboratory (Alpha Analytical; Mansfield, MA) that analyzed most of the natural resource trustees’ samples. These two factors allow for direct comparisons to the detailed chemical characteristics of the fresh Macondo oil, the floating Macondo oils, and the NRDA environmental samples analyzed by the same methods at Alpha Analytical.

¹ Shoreline Cleanup Assessment Techniques (2012) SCAT maps, available: <http://gomex.erma.noaa.gov/erma.html>

² These included surface and buried oil layers, sand patties, tarballs, oiled vegetation, Teflon nets (used to collect liquid oil or to wipe oil coatings from solid surfaces) and oiled debris (wood and plastic).



Previous Studies – Stranded Macondo Oil Weathering

Several existing studies report on the chemical composition of limited numbers of stranded Macondo oils collected in the spring, summer, or fall of 2010 (OSAT 2011, Aeppli et al., 2012; Liu et al., 2012; Kiruri et al., 2013; Hall et al., 2013; Aeppli et al., 2014; Gros et al., 2014; Overton et al., 2014; Lewan et al., 2014). These studies collectively showed the stranded oils experienced compositional changes consistent with weathering. The most obvious change was the loss of the volatile fraction ($< \sim n\text{-C}_{15}$), which based on the survey of floating Macondo oils (Stout, 2015a) predominantly occurred prior to the oil actually reaching shorelines. The severity of evaporation of stranded oils in these studies largely “masked” any dissolution of soluble constituents (most of which are also relatively volatile). However, some dissolution was reportedly evident in the preferential reduction of more soluble compounds (e.g. phenanthrene) over less soluble compounds (e.g., alkyl-phenanthrenes; Aeppli et al. 2012).

The previously studied stranded oils showed an increase in the percent mass of oxygenated hydrocarbons (Aeppli et al. 2012; 2014; Hall et al. 2013; McKenna et al. 2013; Kiruri et al. 2013; Radovic et al. 2014). The increase was attributed in part to enrichment (as hydrocarbons are removed via evaporation or dissolution), but mostly to the formation of “new” oxygenated hydrocarbons through both photo-oxidation and biodegradation (Aeppli et al. 2012). Notably, upon inspection of the data presented by Aeppli et al. (2012) one sees that the increase in oxygenated hydrocarbons was most dramatic in floating oils, which did not yet show evidence of biodegradation but did show evidence of photo-oxidation. Therefore, in my opinion, photo-oxidation appears to be the dominant process in the formation of the oxygenated hydrocarbons among stranded oils. Regardless of how they form, the formation of oxidized oil residues is considered significant as these can be more toxic than the parent hydrocarbons (e.g., Maki 2001).

Previous Studies – Stranded Macondo Oil Distribution

The Shoreline Cleanup Assessment Techniques (SCAT) program provided the exhaustive assessment of the spatial distribution (and degree; e.g., heavy to trace) of stranded Macondo oil in the months following the *Deepwater Horizon* oil spill (Michel et al., 2013). Based upon visual observations of the orangish-brown Macondo oil/emulsion (e.g., Fig. 1), SCAT reported that ~1770 kilometers of shoreline comprised of 50.8% beach, 44.9% marsh, and 4.3% (mostly) man-made shoreline was impacted by stranded Macondo oil. More than 60% of the total oiled shoreline (and nearly 95% of the oiled marsh shoreline) occurred in Louisiana, with the balance observed in Florida (16.1%), Mississippi (14.6%), and Alabama (8.7%). No SCAT reconnaissance occurred in Texas. Separate subsequent Trustee surveys to characterize the linear extent of oiling found that oiling occurred on at least 2,113 kilometers of shoreline (Nixon et al 2015).

Although no chemical fingerprinting analyses were conducted to confirm the visual observations during the SCAT program, some chemical fingerprinting of stranded oils was conducted by BP concurrent with the SCAT program, mostly within what was referred to as the Forensics Rapid Assessment Team-Rapid Assessment Team (FRAT-RAT) program. Results from this program report at least 411 (mostly stranded) “weathered MW-252 crude oil” samples collected in 2010 spanned nearly 500 miles shoreline from Pensacola Bay, Florida to Galveston Bay, Texas (Fig. 2; BP 2014). The highest resolution sampling occurred in Louisiana’s Barataria and Terrebonne Bays. Chemical fingerprinting on limited numbers of tarballs collected mostly from Alabama and Mississippi shorelines in 2010 further confirmed the widespread occurrence of stranded Macondo oil (Rosenbauer et al. 2010; Mulabagal et al. 2013). Based upon these studies (and those referenced above; *Previous Studies – Stranded Oil Weathering*) the ability to recognize Macondo oil was primarily based upon petroleum



biomarkers (specifically, triterpanes and steranes), whose distributions were not altered by the weathering the stranded oil had experienced in 2010. This same approach is employed in this study.

Samples and Methods

Samples

The population of 1333 stranded oils considered herein included tarball, patties, oil mats (all with varying amounts of sand), oiled vegetation, Teflon nets (used to collect liquid oil or to wipe oil coatings from solid surfaces)³ and oiled debris (wood and plastic) collected from the supra-tidal and intertidal portions of shorelines in Louisiana, Alabama, Mississippi, and Florida between May 24 and November 14, 2010. The stranded oil samples were collected by walking shorelines or by wading ashore from small boats. The location of each sample was recorded using hand-held GPS units and photographs of the samples in situ were taken prior to placing the samples into clean glass jars. All samples were collected as part of the NRDA effort following normal chain-of-custody procedures. Attachment 1 to this report contains an inventory of the 1333 samples.

All of the samples were stored on ice (<4°C) and shipped cold to Alpha Analytical (Alpha; Mansfield, Massachusetts) shortly after being collected. Upon receipt all samples were stored in the dark and frozen (-20°C) until analysis.

Sample Preparation and Analytical Methods

Aliquots of stranded oil samples containing varying amounts of sand were diluted in dichloromethane (DCM) and then processed through glass fiber filter and sodium sulfate. An aliquot of the filtered extract was then spiked with surrogate internal standard (SIS) and recovery internal standards (RIS) prior for instrument analysis. The oil adhered to Teflon nets, vegetation, and other debris was rinsed from their surface using DCM. An aliquot was spiked with surrogate internal standard (SIS) and recovery internal standards (RIS) for instrument analysis. Aliquots of each extract were also used to determine the gravimetric weight of the recoverable oil from each sample, thereby allowing the concentrations of target analytes to be reported on an oil weight basis (ug/g_{oil}).

The extracts were analyzed by Alpha in accordance with the AQAP (NOAA 2014). The analyses included:

- (1) *Total Extractable Material (TEM)⁴ and Saturated Hydrocarbon (SHC) Quantification and Fingerprinting:* a modified EPA Method 8015B was used to determine the TEM concentration (C₉-C₄₄) and concentrations of individual *n*-alkanes (C₉-C₄₀) and (C₁₅-C₂₀) acyclic isoprenoids via gas chromatography-flame ionization detection (GC/FID). Concentrations of target compounds are reported in ug/g_{oil} (ppm).
- (2) *PAH, Alkylated PAH and Petroleum Biomarkers:* a modified EPA Method 8270 was used to determine the concentration of (1) approximately 80 PAH, alkylated PAH homologues, individual PAH isomers, and sulfur-containing aromatics and (2) approximately 50 tricyclic and pentacyclic triterpanes, regular and rearranged steranes, and triaromatic steroids via

³ pre-cleaned *Teflon* (TFE-fluorocarbon) nets obtained from General Oceanics (Miami, FL).

⁴ No silica gel cleanup of the sample extracts was performed and therefore, per the AQAP, the mass measured is referred to as TEM as it includes non-hydrocarbons.



GC/MS operated in the selected ion monitoring mode (SIM).
Concentrations of target compounds are reported in ug/g_{oil} (ppm).

The total of 50 PAH and sulfur-containing aromatics ranging from naphthalene to benzo(ghi)perylene (excluding retene and perylene) is reported at TPAH₅₀.

Any TEH, SHC, PAH and biomarker concentrations reported herein are non-surrogate corrected. The analytical results for all 1333 samples were reported through NOAA DIVER, although the concentrations reported therein were surrogate corrected.

Chemical Fingerprinting Methods

The specific character of each of the stranded oils was determined using a tiered oil spill fingerprinting methodology described in detail elsewhere (Stout 2015b). Briefly, this methodology involved the qualitative review of GC/FID chromatograms and quantitative review of 29 diagnostic ratios (DRs) based upon measured concentrations of PAHs and petroleum biomarkers. The samples were each classified into one of five categories "A" through "E", as defined in Table 1. In practice, Macondo oil was considered to be comprise or be present in all of the stranded oil samples classified as A or B (Table 1).

It is notable that these same five classifications (A, B, C, D, and E) have been used throughout the NRDA's investigation chemical fingerprinting conducted by NewFields as a means to standardize the classification terminology for all matrices (oily matrices, sediments, and tissues) in regard to the impact/presence of Macondo oil.

Degree of Weathering Quantification

The degree of weathering in each of the stranded oils comprised of Macondo oil (i.e., fingerprint classifications of A or B; Table 1) was determined based upon mass losses relative to the conservative internal marker within the oil, viz., 17 α (H),21 β (H)-hopane (referred to hereafter as "hopane"), which has proven recalcitrant to biodegradation (Prince et al., 1994) and photo-oxidation (Garrett et al., 1998). This approach was used to estimate the percent total depletion of the C₅+ liquid oil (C₁-C₄ gases excluded) using the following formula:

$$\% \text{Total Oil Depletion} = [1 - (H_0/H_s)] \times 100 \quad \text{Eq. (1)}$$

where H₀ and H_s are the concentrations of hopane in the average, fresh Macondo source oil (68.8 $\mu\text{g/g}$; Stout, 2015c) and stranded oil sample, respectively. The percent depletion of any given fraction (e.g., TPAH₅₀) or individual chemicals (e.g., naphthalene) in the stranded oils was estimated using the following formula:

$$\% \text{Depletion of A} = [((A_0/H_0) - (A_s/H_s))/(A_0/H_0)] \times 100 \quad \text{Eq. (2)}$$

where A_s and H_s are the concentrations of the target analyte and hopane in the stranded oil sample, respectively, and A₀ and H₀ are the concentrations of the target analyte and hopane in the average, fresh Macondo source oil. Although hopane can be degraded under some circumstances, if it (H_s) were in a given sample any % depletions calculated are underestimated.

As is common practice, and in order to eliminate the effects of varying surrogate recoveries on the %loss calculations, non-surrogate corrected concentrations are used



in all calculations. Total oil depletion and individual mass losses calculated by these methods account only for mass loss from the liquid oil, i.e., they do not account for mass losses of gases (C₁-C₄) originally present in the Macondo oil.

Results and Discussion

Stranded Oil Chemical Fingerprinting

Chemical fingerprinting of the 1333 stranded oil samples resulted in their classifications as defined in Table 1. Individual sample results are given in Attachment 1. In summary:

- 1188 of the stranded oil samples (89.1%) were consistent with Macondo oil and were given a classification of A.
- 31 of the stranded oil samples (2.3%) were mostly consistent with Macondo oil and were given a classification of B.
- 38 of the stranded oil samples (2.9%) contained too little oil to yield reliable chemical fingerprints and therefore, were given a classification of D.
- 76 of the stranded oil samples (5.7%) were inconsistent with Macondo oil, i.e., derived from another source (classification of E).

Thus, 91.4% of the stranded oil samples studied (or, excluding the D classifications, 94.1% of those containing sufficient oil for fingerprinting) were determined to be comprised of or contain Macondo oil. Most samples warranting a B classification were the result of low oil concentrations and/or interferences from natural organic matter, which though Macondo oil was clearly present (e.g., GC/FID chromatogram), numerous diagnostic ratios (DRs) were altered or not calculable.

Only 5.7% of the 1333 stranded oil samples (or, excluding the 38 D classifications, 5.9% of the 1295 samples containing sufficient oil for fingerprinting) were comprised of non-Macondo oils. Notably, 20 of these (1.5% of all samples) were associated with the Mud Lake oil spill that occurred in northwestern Barataria Bay in July 2010.⁵ The remaining 56 stranded oils derived from other sources that included (1) a variety of crude or heavy fuel oils often derived from “foreign” oil (i.e., non-South Louisiana Crude Oil Family), (2) numerous wax-rich heavy oils recognized as typical of illegal tank cleaning and ballast discharges from tankers and, (3) pyrogenic tar-like materials (e.g., coal tar or weathered creosote). The GC/FID chromatograms for examples of each of these types of non-Macondo stranded oils are shown in Figure 3.

The low percentage of non-Macondo oils among the stranded oil dataset is primarily due to bias in the sampling, which had focused on collecting samples that visibly appeared to be comprised of Macondo oil (e.g., orangish-brown colored oils, as in Fig. 1). The 56 non-Macondo (and non-Mud Lake spill) oils were often hard, black asphalt-like tarballs, such as were recognized in an earlier survey of tarballs from the region (Henry et al. 1993). In this earlier study, a survey of Louisiana shorelines in 1992 found tarballs believed to derive from both natural and anthropogenic sources. The latter were considered most common and included heavy fuel oils and “foreign” crude oil (e.g., Middle East and Alaskan North Slope) believed to be derived from illegal tank cleaning

⁵ The Mud Lake spill was caused by a blowout that occurred July 27, 2010 after a barge/vessel (T/V Pere Ana C) struck an active wellhead in northwestern Barataria Bay. Twenty samples were collected July 30th from the spill area and analyzed as part of the NRDA. The distinct character of this oil was previously described by Stout (2015b).



and ballast discharges from tankers. Over 80% of the stranded oils surveyed in 1992 were hard, black tarballs, which would be considered visibly distinct from the liquid-to-pliable orangish-brown stranded Macondo oil found on northern Gulf of Mexico shorelines throughout 2010 (e.g., Fig. 1). The chemical character of all 76 non-Macondo oils encountered in the present study was not considered further.

Extent of Stranded Macondo Oils in 2010 Determined by Chemical Fingerprinting

The spatial distribution of the 1219 stranded oil samples derived from Macondo oil (Class A and B) and the 76 from non-Macondo oils (Class E) are shown in Figure 4. Inspection of these maps reveals that stranded Macondo was present on shorelines spanning approximately 500 miles from western Terrebonne Bay, Louisiana to western Apalachicola Bay, Florida. The easternmost and westernmost samples collected were comprised of Macondo oil indicating the full eastern and western extents are not likely represented by the 1333 samples collected. Evidence in support of this is the reported presence of “weathered MC-252 oil” in stranded oils collected to the west of the NRDA sample set perhaps as far west as Galveston Bay (as reported by BP; Fig. 2).

In Louisiana, the fingerprinting results confirm that Macondo oil reached Grande Isle and other offshore islands, marshes deep within Terrebonne, Timbalier, and Barataria Bays (Fig. 4A), marshes throughout the eastern delta area (Fig. 4B), Chandeleur Island (Fig. 4C), and the birdfoot delta area. The extent of the 20 non-Macondo oil derived from the Mud Lake blowout (Stout, 2015b) can be seen in NW Barataria Bay (Fig. 4A). Notably, stranded oils that were derived from Macondo oil were found in and around the Mud Lake area, but these samples were collected in June 2010, i.e., about 1 month prior to the Mud Lake blowout.

In Mississippi and Alabama, the fingerprinting results confirm the presence of Macondo oil in coastal beaches across both States, as well as the Gulf Islands National Seashore (i.e., Cat, West Ship, East Ship, Horne, Petit Bois, and Dauphin Islands; Fig. 4D). It is perhaps notable that stranded Macondo oil was found on both the Gulf and landward sides of most of these islands.

In Florida, the fingerprinting results demonstrate the Macondo oil was found on shorelines within the Big Lagoon, Pensacola Naval Air Station, and the landward side of Gulf Islands National Seashore, i.e., Macondo oil entered the mouth of Pensacola Bay (Fig. 4E). Coastal beaches east of Pensacola were also impacted with Macondo oil at least as far as Apalachicola Bay, the easternmost location where NRDA stranded oil sampling occurred (Fig. 4F).

Spatial Extent of Shoreline Oiling - Chemical Fingerprinting versus SCAT

The extent of stranded Macondo oil determined through chemical fingerprinting was first qualitatively compared to the extent of maximum oiling determined throughout the SCAT program (Michel et al., 2013). Generally, as might be expected, it was observed that shorelines recognized during SCAT to have experienced heavy-to-moderate oiling were also shown to contain stranded Macondo oil. However, the opposite was not necessarily true. Specifically, the qualitative comparison revealed many shorelines where the SCAT program's maximum oiling category (i.e., highest degree of oiling ever observed on a shoreline; Michel et al., 2013) was “*no observed oil*”, yet chemical fingerprinting revealed Macondo oil was present on these same shorelines.



Therefore, a more quantitative, GIS-based comparison was performed in which the locations and frequency of the 1219 stranded Macondo oil samples (i.e., fingerprinting class A or B) collected from “no observed oil” shorelines were determined. Results show that the majority of stranded Macondo oil samples (1029 samples; 84%) were collected from shorelines which SCAT had recognized to be visibly impacted to some (e.g., heavy, moderate, light, very light, or trace maximum oiling categories; Michel et al., 2013). However, the comparison revealed that 190 of the 1219 stranded Macondo oil samples (16%) were collected from shorelines where the SCAT program had reported “no observed oil”.

Figure 5 shows the locations of these 190 stranded Macondo oils (confirmed by chemical fingerprinting) that were collected from shorelines where SCAT had reported no oil was observed. There are examples found throughout the study area but several notable “clusters” of samples exist in a few areas. For example, the landward side of Timbalier Island (Fig. 5A), western Barataria Bay (Fig. 5B), the eastern delta area (Fig. 5C), Grand Bay (west of Mobile Bay), and the Apalachicola Bay area (Fig. 5D) each had multiple stranded Macondo oil samples collected from shorelines not recognized by SCAT to have been impacted.

The SCAT program’s objectives were to assess oiling conditions and support decision making on appropriate cleanup methods, which it accomplished quite well (Michel et al., 2013). However, this comparison (Fig. 5) shows that SCAT did not necessarily represent the full extent to which shorelines were impacted by stranded Macondo oil. Thus, while chemical fingerprinting of most of the stranded Macondo oils 1029 samples; 84%) support/confirm the SCAT program assessments, chemical fingerprinting of some stranded Macondo oils (190 samples; 16%) supplements and extends the shorelines impacted by stranded Macondo oil.

Range of Weathering among Stranded Oils

Weathering collectively reduces the mass of oil, which is reflected total oil depletion calculable by Equation (1). The percent total oil depletion (C_5+) among the 1188 stranded Macondo oils (fingerprint class A’s)⁶ ranged from 25% to 80% and averaged $55 \pm 6.2\%$ total mass loss. Thus, on average, the stranded oils collected from shorelines in 2010 contained only $45 \pm 6\%$ of the C_5+ mass of the oil originally released at the wellhead. (Remember this mass loss does not include C_1 to C_5 gases.) This mass loss is, on average, 17% higher than exhibited by the population of floating Macondo oils in 2010 (15% to 52%, avg. $38\% \pm 9\%$; Stout, 2015a). Thus, on average, there was an additional 17% total mass loss from floating Macondo oils that occurred during the oil’s transport to and/or after becoming stranded on shorelines. The weathering processes responsible for the additional mass loss are discussed in the next section.

One might assume that the later in 2010 that a sample was collected, or the further away from the wellhead that a sample was collected, the more highly weathered the Macondo oil was likely to be. This assumption is not well supported by the large sample set studied, which show the percent total oil depletion versus date of collection and distance from the wellhead for the 1188 stranded Macondo oils (Fig. 6). Despite slight overall increases in weathering with increasing time and distance, both plots show there to be

⁶ Fingerprint class B are not included since, despite containing Macondo oil, many of these samples are affected by interferences and/or dilution from natural organic matter.



significant scatter (and low correlation coefficients) revealing no clear relationship between the extent of weathering and the collection date or distance from the well.

Sampling date, of course, does not likely represent the day the oil actually arrived on the shoreline and there is no way to know how long a stranded oil sample had resided on the shore prior to collection. Therefore, the lack of any obvious relationship between weathering and collection date throughout 2010 might be expected (Fig. 6A).

Distance from the wellhead, however, does truly reflect how far the stranded oil traveled as a floating oil before reaching a shoreline yet there is still no obvious relationship between distance from the wellhead and degree of weathering (Fig. 6B). The samples collected only 50 to 60 miles from the wellhead (i.e., the Mississippi River birdfoot area) exhibit a comparable range in weathering as the samples collected nearly 200 miles from the wellhead (i.e., Apalachicola Bay area). This result serves to emphasize that the rate(s) of weathering of (floating and) stranded Macondo oil in 2010 was a complex process that cannot be reliably predicted based a stranded oil sample's location (or collection date).

Chemical Composition of Stranded Oils

As noted above, the percent total depletion for the stranded Macondo oils found on shorelines in 2010 ranged from 25% to 80% and averaged $55 \pm 6.2\%$. In this section the specific chemical compositions of the stranded oils are discussed so that an understanding of what specific chemicals were depleted and what weathering processes were likely responsible for their loss. Oppositely, the chemicals that were retained in the stranded oils are relevant to understanding what the resources in the region's beach and marsh ecosystems were actually exposed to in the months following the spill.

BTEX in Stranded Oils: Figure 7 shows the GC/FID chromatograms for two stranded oils that exemplify the range in weathering among the 1188 stranded Macondo oil (fingerprint class A's). The most obvious feature of these chromatograms is the absence of detectable compounds present below $n\text{-C}_{13}$ in even the least weathered of the stranded oils (Fig. 7B). Although none of the stranded oils were analyzed specifically for volatile hydrocarbons, the absence of compounds below $n\text{-C}_{13}$ argues the stranded oils apparently contained no detectable concentrations of benzene, toluene, ethylbenzene or xylenes (BTEX).

As discussed elsewhere, the loss of BTEX from the Macondo oil is expected to have initiated via dissolution and biodegradation in the deep ocean (Reddy 2012; Hazen 2010). Evaporation is likely to have further depleted any BTEX in oil that reached the surface water. The absence of BTEX from stranded Macondo oil is not surprising given the low concentrations of any BTEX compounds detected in floating Macondo oils (non-detect to $5.9 \mu\text{g/g}$) and the expectation for continued loss during transport to, or upon reaching, shorelines.

n-Alkanes in the Stranded Oils: Even the least weathered stranded oil encountered had experienced a 25% total mass loss (see above), which based upon the n -alkane profile, indicates complete loss of compounds below $n\text{-C}_{13}$ with at least some losses extending up to about $n\text{-C}_{20}$ (Fig. 7B and inset). The unresolved complex mixture (UCM) "hump", which contains complex mixture of branched, cyclic, and aromatic hydrocarbons exhibits a comparable loss, also extending up to about $n\text{-C}_{20}$ (Fig. 7B). Because the percent depletion among n -alkanes tends to decrease with increasing carbon number (i.e.,



decreasing vapor pressure), and because the UCM exhibits the same progressive losses as n-alkanes, evaporation is considered the primary weathering process responsible for loss of most mass below about n-C₂₀. This same conclusion had been previously reached for floating Macondo oils (Stout, 2015a) and by other researchers studying smaller populations of stranded Macondo oils from 2010 (OSAT 2011, Aeppli et al., 2012; Liu et al., 2012; Kiruri et al., 2013; Hall et al., 2013; Aeppli et al., 2014; Gros et al., 2014; Overton et al., 2014).

As weathering progressed the most weathered stranded Macondo oils exhibiting up to 80% total mass depletion (see above) tend to exhibit a complete (100%) loss of compounds below ~n-C₁₅ with at least some depletion of n-alkanes extending all the way up to n-C₃₀ (Fig. 7C and inset). The most highly weathered floating Macondo oils had exhibited only minor (<20%) depletion of long chain (C₂₅+) n-alkanes, which was attributed to severe evaporation given the high air temperatures (25-30°C) and high solar radiation during the spill.

Although severe evaporation likely also contributes to somewhat higher depletion of long chain n-alkanes in the most weathered stranded oils (>60%), biodegradation appears to be a contributing factor. Specifically, many of the most weathered stranded oils exhibit lower percent depletions for the less biodegradable acyclic isoprenoids (pristane and phytane) relative to more biodegradable n-alkanes (n-C₁₇ and n-C₁₈; inset Fig. 7C). (If the percent depletions were comparable between isoprenoids and n-alkanes, such as in Fig. 7B, evaporation alone is responsible for the depletions.) This difference indicates biodegradation had commenced in at least some of the stranded oils in 2010. Because biodegradation was not evident among the floating oils from the spring and summer of 2010 (Stout, 2015a), the initiation of biodegradation in some of the more severely weathered stranded oils in 2010 indicates favorable conditions (e.g., nutrients and surface area exposure; Prince et al., 2013) for biodegradation were achieved upon reaching shorelines (but were not available in the undispersed floating oils collected from the Gulf).

Polycyclic Aromatic Hydrocarbons in the Stranded Oils: Table 2 contains the average, minimum, and maximum concentrations of the PAH and related compounds (e.g., decalins and sulfur-containing aromatics) measured in the population of stranded Macondo oils studied. The average concentrations of PAH in fresh Macondo oil (Stout, 2015c) are given for comparison.

The average concentrations of total PAHs (expressed as TPAH₅₀) in the fresh and stranded Macondo oils are given at the bottom of Table 2. In summary,

- the concentration of TPAH₅₀ in fresh Macondo oil was 13,251 µg/g.
- the concentration of TPAH₅₀ in stranded Macondo oils averaged 1707 ± 747 µg/g and ranged from 333 to 8254 µg/g.

This means that the stranded Macondo oils had experienced a depletion of TPAH₅₀ that averaged 94 ± 3.1% and ranged from 67 to 99%. Though calculated using less than 50 PAH analytes, the OSAT-II reported 30 stranded Macondo oils collected between October 2010 and January 2011 had similarly lost between 86 and 98% of the total PAHs present (OSAT, 2011). Similarly, Aeppli et al. (2012) reported stranded Macondo oils collected in 2011 had lost between 83 and 98% of total PAHs. Thus, the “freshest”



of the stranded oils encountered in this study were the “freshest” stranded oils studied (to my knowledge).

The concentrations of TPAH₅₀ in the stranded Macondo oils are less than previously reported for floating Macondo oils (6640 ± 4140 $\mu\text{g/g}$ and ranged from 1010 to 13,700 $\mu\text{g/g}$; Stout, 2015a). These had corresponded to a depletion of TPAH₅₀ that averaged $69 \pm 23\%$ and ranged from 12 to 96%). This means that the stranded oils studied herein experienced additional losses of PAH compared to the floating oils during their transport to, or upon reaching, shorelines.

Figure 8 shows hopane-normalized histograms for PAHs and related compounds in a minimally-weathered, average, and severely-weathered stranded oil, and versus those of fresh Macondo oil. (The representative minimally- and severely-weathered stranded oils shown are the same samples as were depicted in Figure 7.) Also given in Figure 8 are the TPAH₅₀ concentrations and their percent depletions relative to hopane (per Eq. 2).

Inspection reveals that minimally-weathered stranded Macondo oil had experienced a 67% depletion in TPAH₅₀ (Fig. 8A). Most of this depletion is attributable to the loss of naphthalene (N0) and alkylated naphthalenes (N1-N4), most likely due to the combined effects of evaporation and dissolution (Fig. 8A). Fluorenes and phenanthrenes are also reduced with each parent PAH exhibiting greater reductions than the more highly alkylated PAHs. These reductions would also be consistent with evaporation and dissolution. Biodegradation is also possible but seems unlikely at this level of weathering, i.e., n-alkanes do not exhibit evidence of biodegradation yet affecting this sample (e.g., Fig. 7A; see above). (This is perhaps not surprising since this sample was one of the earliest stranded oil samples collected; May 28, 2010.) Interestingly, the opposite pattern is evident among the chrysenes (C0-BC4), wherein the more highly alkylated chrysenes are depleted to a greater degree than the parent chrysene (Fig. 8A inset). This will be discussed further below.

On average, the 1188 stranded Macondo oils studied contained 1707 ± 747 $\mu\text{g/g}$ TPAH₅₀ (Table 2), which as noted above, corresponds to a $94 \pm 3.1\%$ depletion of total PAHs relative to hopane (Eq. 2; Fig. 8B). Because most stranded oils were severely weathered, the individual severely weathered stranded oil shown in Figure 8C closely resembles the average stranded oils (Fig. 8B), and exhibits only slightly lower TPAH₅₀ concentration (1535 $\mu\text{g/g}$) and slightly higher percent depletion of TPAH₅₀ (94%).

Lower molecular weight PAHs (LPAHs) such as naphthalenes and fluorenes are nearly completely absent from most stranded oils causing phenanthrenes, although depleted themselves, to become the dominant PAHs present (Fig. 8B-C). Most higher molecular weight PAHs (HPAHs) are also depleted and most homologous profiles show a shift toward PAHs with higher degrees of alkylation. For example, C4-fluoranthrenes/pyrenes (FP4) have become the dominant homologue among the FP series (Fig. 8B-C). However, a different profile is evident within the naphthobenzothiophene (NBT0-NBT4) and benzo(a)anthracene/chrysene homologues (C0 to BC4) in which the methyl-homologues (NBT-1 and BC1) have become dominant (Fig. 8B-C insets). This atypical pattern was also evident in the minimally weathered stranded oil (Fig. 8A inset).

These atypical homologue patterns were also observed in the more highly weathered floating Macondo oils (Stout, 2015a) and are likely to be due to the effects of photo-



oxidation. Specifically, while biodegradation is considered to progress slower with increased degree of alkylation (Elmendorf et al. 1994), photo-oxidation is considered to progress faster with molecular size and degree of alkylation (Prince et al., 2003); (Maki et al., 2001, Garrett et al., 1998). Thus, the skewing of the naphthobenzothiophenes and benzo(a)anthracene/chrysene homologues toward the left in the stranded oil (Fig. 8 insets) are consistent with changes caused by photo-oxidation.

The effects of photo-oxidation on floating and stranded Macondo oil have also been recognized by other researchers (Aeppli et al., 2012; Radovic et al., 2014). Aeppli et al. (2012) show that oxidized hydrocarbons (in part formed via photo-oxidation) comprised more than 50% of the mass of stranded Macondo oils collected throughout 2011 (somewhat later than the stranded oils studied herein). Establishing that photo-oxidation has affected the floating and stranded Macondo oils is important because the process has been associated with increased toxicity of seawater in contact with photo-oxidized oils (e.g., Lee et al., 2003; King et al., 2014).

The depletion of most individual PAH analytes and analyte groups in minimally-weathered, average, and severely-weathered stranded oil, versus those of fresh Macondo oil can be seen in Figure 9. (The minimally- and severely-weathered oils shown are the same as were depicted in Figures 7 and 8.) These graphs show the progression in weathering of the stranded oils with the minimally-weathered oil exhibiting greater depletion among the less alkylated LPAHs, dominated by losses of decalins, benzothiophenes, naphthalenes, phenanthrenes, and dibenzothiophenes (Fig. 9A). These losses are mostly consistent with evaporation although dissolution is also likely. This minimally-weathered stranded oil sample did not yet exhibit evidence of biodegradation (Fig. 7A), and therefore, this weathering process seems unlikely to have contributed to the PAH depletions in this sample.

As weathering of the stranded Macondo oils progressed it is clear that all of the LPAH and HPAH groups are increasingly depleted (Fig. 9B-C). On average, the stranded Macondo oils exhibit a predictable pattern of PAH weathering in which the percent depletions within most homologue groups decreases with increasing degree of alkylation (see downward pointing arrows in Fig. 9B-C). This is clearly evident in all of the homologue groups between decalins (D0-D4) and fluoranthrenes/pyrenes (FL0-FP4). In addition, these depletions tend to decrease with increasing ring number so that, for example, the depletion among naphthalenes exceeds those of fluoranthrenes/ pyrenes with losses among phenanthrenes/ anthracenes and dibenzothiophenes being intermediate and mostly equal. As the stranded oils became severely weathered the depletion of all LPAH and fluoranthrenes/ pyrenes increased becoming nearly complete (68 to 100%; Fig. 9C). These trends are consistent with the combined effects of dissolution, evaporation, and, in the case of the more severely weathered stranded oils, biodegradation.

Among the HPAHs, notably, benz(a)anthracene is markedly depleted (73%) and eventually becomes completely depleted (100%), whereas its isomer chrysene is far less depleted (51%; Fig. 9C). This different response among these HPAH isomers is also consistent with photo-oxidation, which has a greater effect on benz(a)anthracene due to its peri-condensed molecular structure and larger cross-sectional area (Plata et al., 2008).



The other HPAH homologue groups, i.e., naphthobenzothiophenes and benz(a)anthracenes/chrysenes, exhibit greater depletion among the more alkylated homologues (Fig. 9). This, of course, is consistent with their atypical homologue patterns (insets to Fig. 8; described above) and is also caused by photo-oxidation of the more highly alkylated benz(a)anthracenes/chrysenes (Prince et al., 2003; Maki et al., 2001; Garrett et al., 1998). The lack of depletion among naphthobenzothiophenes in the minimally weathered stranded oil (Fig. 9A) suggests that benz(a)anthracenes/chrysenes are initially more susceptible to photo-oxidation than the naphthobenzothiophenes. With advancement in weathering, however, the depletion of naphthobenzothiophenes and benz(a)anthracenes/chrysenes become more or less comparable (Fig. 9B-C).

Biomarkers in the Stranded Oils: The stability of biomarkers during weathering of spilled oil is a fundamental basis for their use in chemical fingerprinting (Wang et al. 2006). The stranded Macondo oils exhibited mostly stable triterpane and sterane biomarker distributions regardless of the degree of weathering, which allowed for the use of numerous biomarker-based diagnostic ratios (DRs) in “fingerprinting” these oils (Stout, 2015b).

Despite the stability demonstrated among triterpanes and steranes, the most severely weathered of the floating oils from 2010 had exhibited marked reduction in the abundance of triaromatic steroid (TAS) biomarkers (Stout, 2015a). Error! Bookmark not defined. The four TAS congeners had exhibited percent depletions that narrowly range from 58 to 62% relative to hopane (Eq. 2), which indicated the process(es) responsible for their depletion has affected all four congeners similarly. Like the HPAHs described above, the reduction in TAS in severely weathered floating oil was attributed to photo-oxidation of these aromatic biomarkers, which had also been observed in spilled and laboratory irradiated Macondo oils (Aeppli et al., 2014; Radovic et al., 2014).

Not surprisingly the stranded Macondo oils studied herein also exhibit a reduction in TAS, which can be visualized in Figure 10. However, unlike the floating oils where only the most severely weathered examples were depleted in TAS, all of the stranded oils studied exhibit marked depletion of all four TAS congeners. This indicates that photo-oxidation of the TAS had advanced during transport to, or upon reaching, shorelines. The distributions and abundances of the individual triterpanes (T4 to T35) and steranes (S4 to S27) in the stranded oils were unaffected by photo-oxidation (or other weathering processes) and closely matched those in the fresh oil (Fig 10).

Dispersant Indicators in the Stranded Oils: Three of the 62 floating oils analyzed contained detectable concentrations of the dispersant indicator di(propyleneglycol)-n-butyl ethers (DPnBs) above the reporting limit that were not “blank qualified” (Stout, 2015a). DPnBs are indicators for Corexit 9500 and their detection in some of the floating oils indicated not all floating oil exposed to dispersants were completely dispersed. This result suggested that at least some “residual” dispersant may have been transported toward shore “encapsulated” in coalesced oil slicks.



A review of the available data for the 1333 stranded oils revealed that only 177 samples were analyzed for dispersant indicators. Only three of these,⁷ all of which were Match A's to Macondo oil, contained detectable concentrations of DPnBs above the reporting limit that were not "blank qualified". All three of these samples were collected from the eastern delta area on July 17, 2010. This result, though limited in scope, suggests some Corexit 9500 may have been transported to shore as a residue in coalesced oil slicks.

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⁷ LAAN42-A0717-B43002 (1007183-14), LAAM42-A0717-B104003 (1007183-03), and LAAM42-A0717-B104011 (1007183-11) contained 2.56, 3.18, and 3.55 µg/g DPnBs, respectively. Concentrations are estimated and not surrogate corrected.



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Table 1: Chemical fingerprinting classification of stranded oil samples.

Fingerprint Classification	Description	Practical Conclusion to NRDA
A	DRs and other features are consistent with weathered Macondo oil	Macondo crude oil is present
B	Most DRs and features are consistent with weathered Macondo oil with any differences being reasonably attributable to low(er) concentrations, the effects of very severe weathering, and/or obvious interferences	Macondo crude oil is present
C	not applied to oily matrices; used in the classification of sediments and tissues where DRs and other features are affected by mixing, interferences, or metabolic effects; other lines of evidence support the possible presence of Macondo oil; Concentrations often low	Macondo crude oil is possibly present
D	data are inconclusive, most often due to a very low concentration of TEM/TPH, PAHs, and biomarkers in the sample	No Macondo crude oil or any other petroleum is obviously present
E	DRs and other features are distinct from weathered Macondo oil and not attributable to weathering and/or mixing (i.e., a different type of oil is present)	Macondo oil is not present but a different petroleum is present

Table 2: Concentrations ($\mu\text{g/g}_{\text{oil}}$) of PAH analytes and hopane in fresh and stranded Macondo crude oils. TPAH50 represents sum of PAHs (N0-GHI, excl. Per.)
Concentrations are non-surrogate corrected.

Abbrev	Analytes	Fresh Macondo	Stranded Macondo Oils (n=1188)			
			Avg	StDev	Min	Max
D0	cis/trans-Decalin	779	0.07	0.42	nd	10
D1	C1-Decalins	1174	0.14	0.86	nd	16
D2	C2-Decalins	966	0.12	1.2	nd	19
D3	C3-Decalins	436	0.07	1.0	nd	25
D4	C4-Decalins	431	0.28	2.8	nd	46
BT0	Benzo(b)thiophene	7.3	0.003	0.05	nd	1.4
BT1	C1-Benzo(b)thiophenes	33	0.06	0.7	nd	18
BT2	C2-Benzo(b)thiophenes	31	0.83	2.1	nd	11
BT3	C3-Benzo(b)thiophenes	48	0.21	1.3	nd	15
BT4	C4-Benzo(b)thiophenes	37	0.40	2.0	nd	26
N0	Naphthalene	964	0.32	0.48	nd	7.7
N1	C1-Naphthalenes	2106	0.69	0.84	nd	20
N2	C2-Naphthalenes	2259	2.5	6.3	nd	118
N3	C3-Naphthalenes	1597	7.1	20	nd	361
N4	C4-Naphthalenes	721	14	24	nd	348
B	Biphenyl	204	0.32	0.29	nd	2.9
DF	Dibenzofuran	30	0.07	0.26	nd	4.2
AY	Acenaphthylene	8.9	0.1	0.38	nd	7.4
AE	Acenaphthene	21	0.05	0.37	nd	11
F0	Fluorene	150	0.92	1.9	nd	32
F1	C1-Fluorenes	308	7.4	12	nd	171
F2	C2-Fluorenes	404	37	33	nd	393
F3	C3-Fluorenes	286	70	39	nd	419
A0	Anthracene	2.3	0.46	1.2	nd	32
P0	Phenanthrene	310	12	18	nd	215
PA1	C1-Phenanthrenes/Anthracenes	676	117	88	1.9	867
PA2	C2-Phenanthrenes/Anthracenes	657	248	127	9.1	1149
PA3	C3-Phenanthrenes/Anthracenes	381	150	74	16	676
PA4	C4-Phenanthrenes/Anthracenes	148	68	30	nd	269
DBT0	Dibenzothiophene	53	1.6	2.5	nd	33
DBT1	C1-Dibenzothiophenes	153	22	19	0.49	192
DBT2	C2-Dibenzothiophenes	197	76	38	2.9	371
DBT3	C3-Dibenzothiophenes	146	83	34	5.6	306
DBT4	C4-Dibenzothiophenes	72	50	19	6.3	176
BF	Benzo(b)fluorene	11	0.14	0.72	nd	9.4
FL0	Fluoranthene	4.1	1.8	7.8	nd	257
PY0	Pyrene	16	4.4	6.6	0.2	197
FP1	C1-Fluoranthenes/Pyrenes	80	23	11	nd	112
FP2	C2-Fluoranthenes/Pyrenes	130	30	16	nd	175
FP3	C3-Fluoranthenes/Pyrenes	158	58	23	13	244
FP4	C4-Fluoranthenes/Pyrenes	125	75	26	18	249
NBT0	Naphthobenzothiophenes	18	18	6.0	nd	50
NBT1	C1-Naphthobenzothiophenes	56	54	17	7.2	138
NBT2	C2-Naphthobenzothiophenes	80	62	21	15	169
NBT3	C3-Naphthobenzothiophenes	58	35	13	nd	116
NBT4	C4-Naphthobenzothiophenes	37	32	13	nd	191
BA0	Benz[a]anthracene	7.3	0.42	3.6	nd	121
CO	Chrysene/Triphenylene	56	59	13	6.1	171
BC1	C1-Chrysenes	129	99	24	21	250
BC2	C2-Chrysenes	158	78	24	19	206
BC3	C3-Chrysenes	156	53	17	17	162
BC4	C4-Chrysenes	90	38	11	nd	95
BBF	Benzo[b]fluoranthene	6.1	6.4	3.9	0.7	125
BJKF	Benzo[jk]fluoranthene	0.5	0.32	3.3	nd	108
BAF	Benzo[a]fluoranthene	nd	0.07	0.8	nd	23
BEP	Benzo[e]pyrene	12	8.8	3.8	1.2	92
BAP	Benzo[a]pyrene	3.2	0.54	3.6	nd	118
PER	Perylene	1.0	0.16	1.1	nd	33
IND	Indeno[1,2,3-cd]pyrene	1.2	0.41	2.7	nd	84
DA	Dibenz[a,h]anthracene	2.5	0.35	1.0	nd	24
GHI	Benzo[g,h,i]perylene	2.3	1.4	2.5	nd	77
	Hopane	69	143	22	37	321
	TPAH50 (Σ N0-GHI) excl. Per	13251	1707	747	333	8254



Figure 1: Photographs of various forms of stranded Macondo oil. (A) sand patty (>10 cm) and tarballs (< 10 cm) on beach surface, (B) buried sand patties exposed on eroded beach face, (C) liquid emulsified oil coating and floating between rocks, (D) dried oil coating rocks, (E) oil on stems of *Spartina alterniflora*, and (F) oil on black mangrove shoots. All photos taken Aug. 24, 2010, Terrebonne-Timbalier Bays area, S.A. Stout.

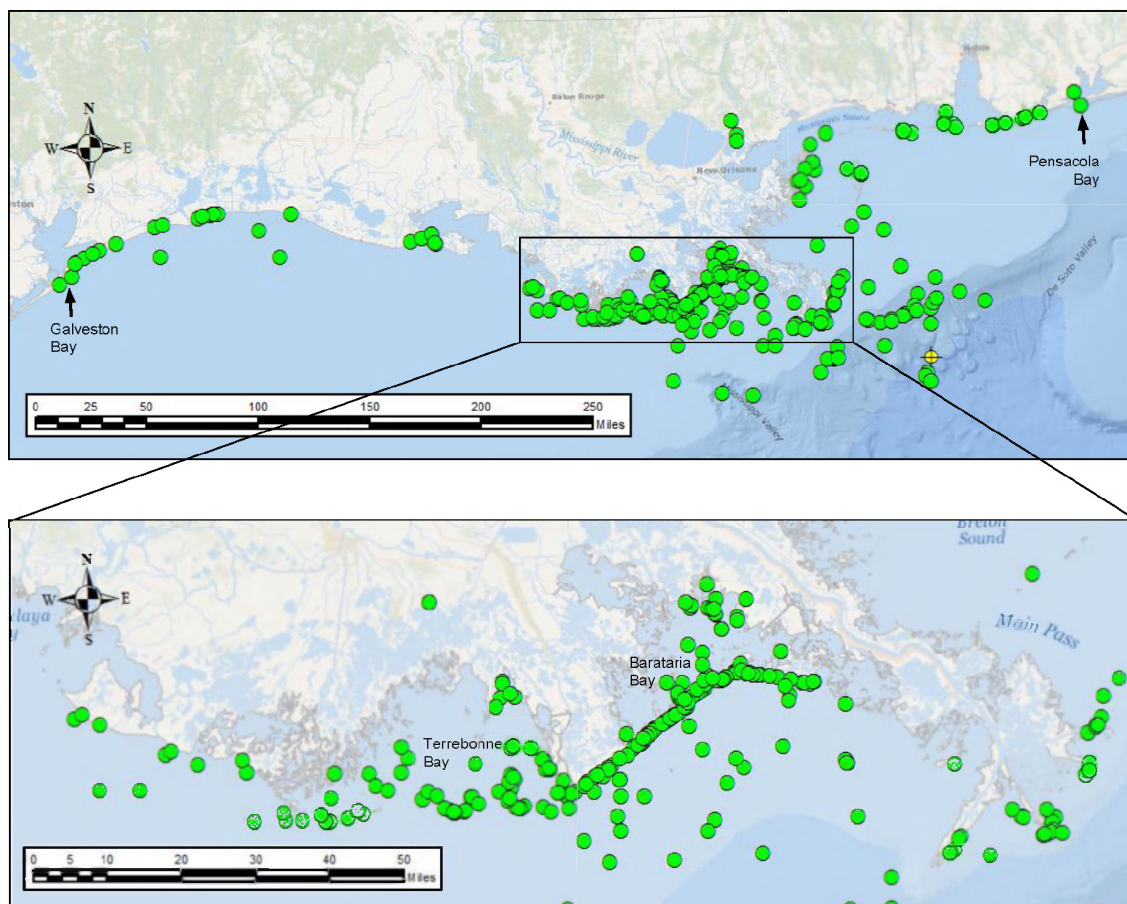


Figure 2: Maps showing the distribution 411 oil samples (May 9-Dec. 15, 2010) chemically fingerprinted and reported by BP to be comprised of “weathered MC-252 crude oil”. Most samples are stranded oils although some floating oils are included. Of particular note is the reported presence of weathered MC-252 oil as far west as Galveston Bay. Data source: BP 2014. Oil Source Interpretations, Ref. No. O-03v-01—01a.zip (Shapefile), BP Gulf Science Data website, Jan. 10, 2014. <http://www.gulfsciencedata.bp.com>.

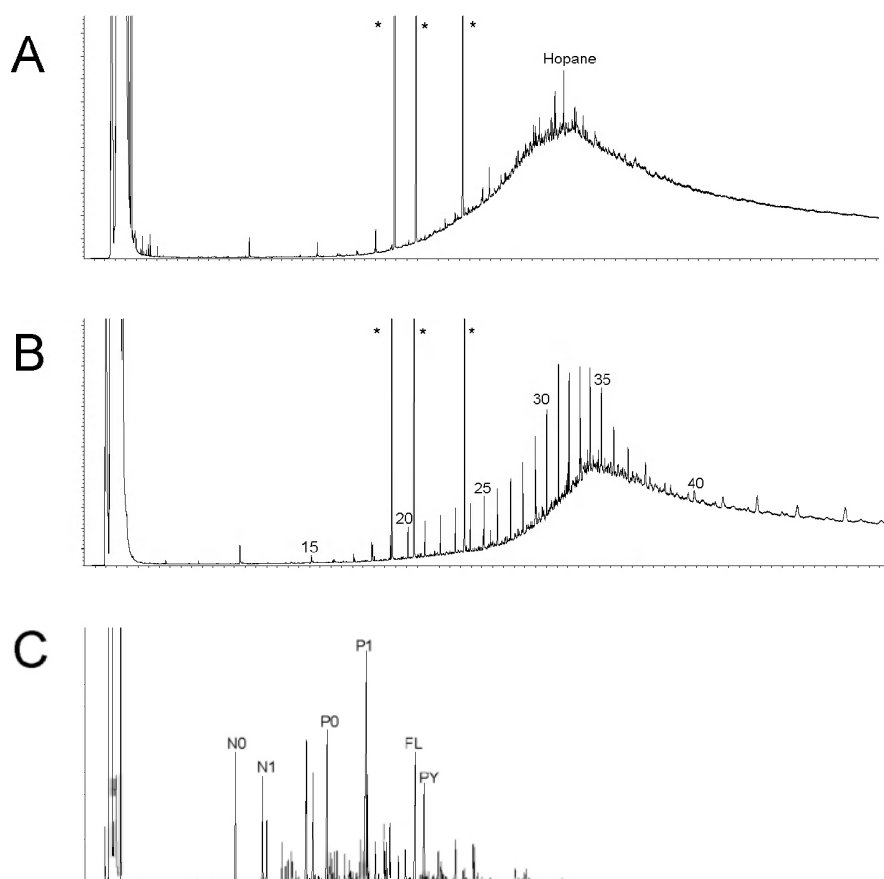


Figure 3: Conventional GC/FID chromatograms for selected stranded oils from non-Macondo sources, i.e., fingerprint classifications of E (Table 1). (A) tarball from Alabama comprised of weathered crude or heavy fuel oil (ALAK48-A0902-BE4005; 1009121-05), (B) wax-rich tarball from Alabama containing likely tank wash oil (ALAK47-A0723-BE5001; 1007220-01), and (C) blackened wood chips from a Mississippi shoreline containing creosote-like material (MSAK42-A0701-BA1002; 1209038-14). * - internal standard; #: *n*-alkane carbon number, NO – naphthalene, N1 – methylnaphthalenes, P0 – phenanthrene, P1 – methylphenanthrenes, FL – fluoranthene, PY – pyrene.

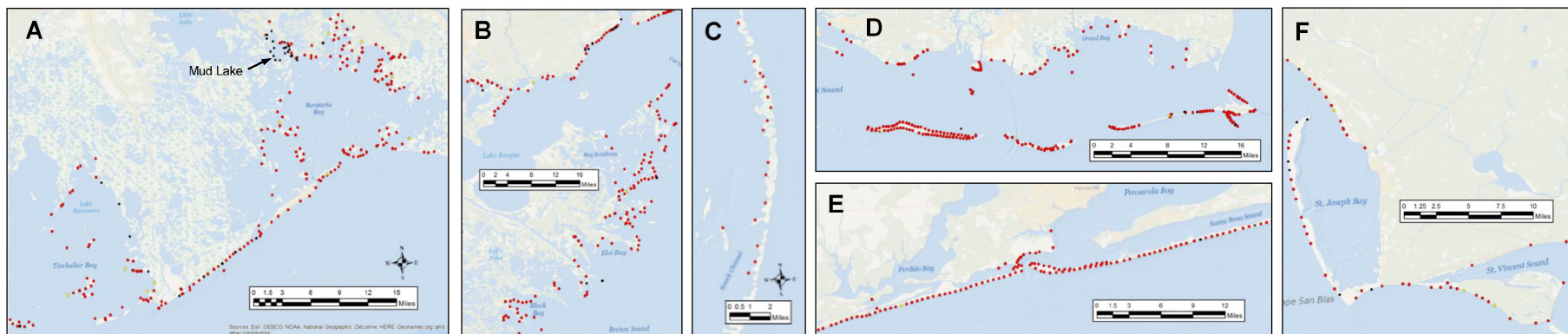
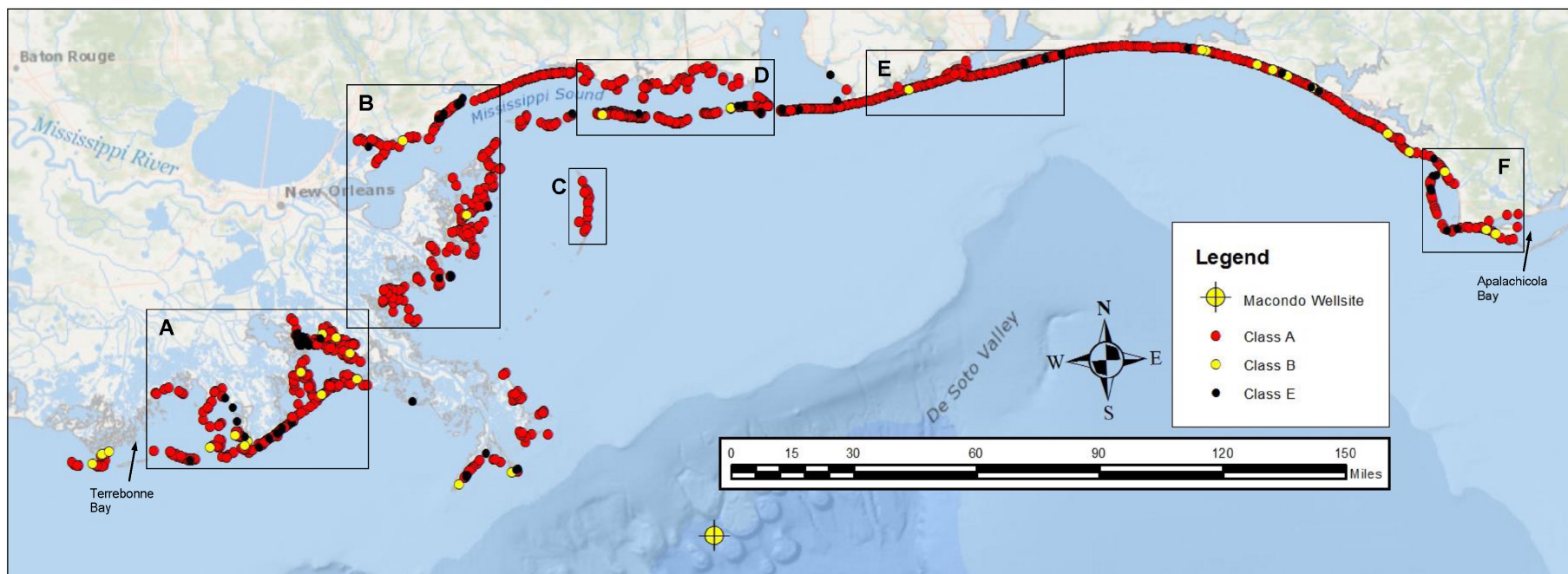


Figure 4: Maps showing the spatial extent of stranded oils from supratidal and intertidal zones collected between May 24 and November 14, 2010 derived from Macondo oil (i.e., Class A and B; n=1188 and 31, respectively) and from non-Macondo oil (i.e., Class E; n=76) as determined by chemical fingerprinting. (A) Timbalier and Barataria Bays area, (B) Eastern delta area, (C) Chandelier Island, (D) Gulf Islands National Seashore area, (E) Pensacola Bay area, and (F) Apalachicola Bay area.

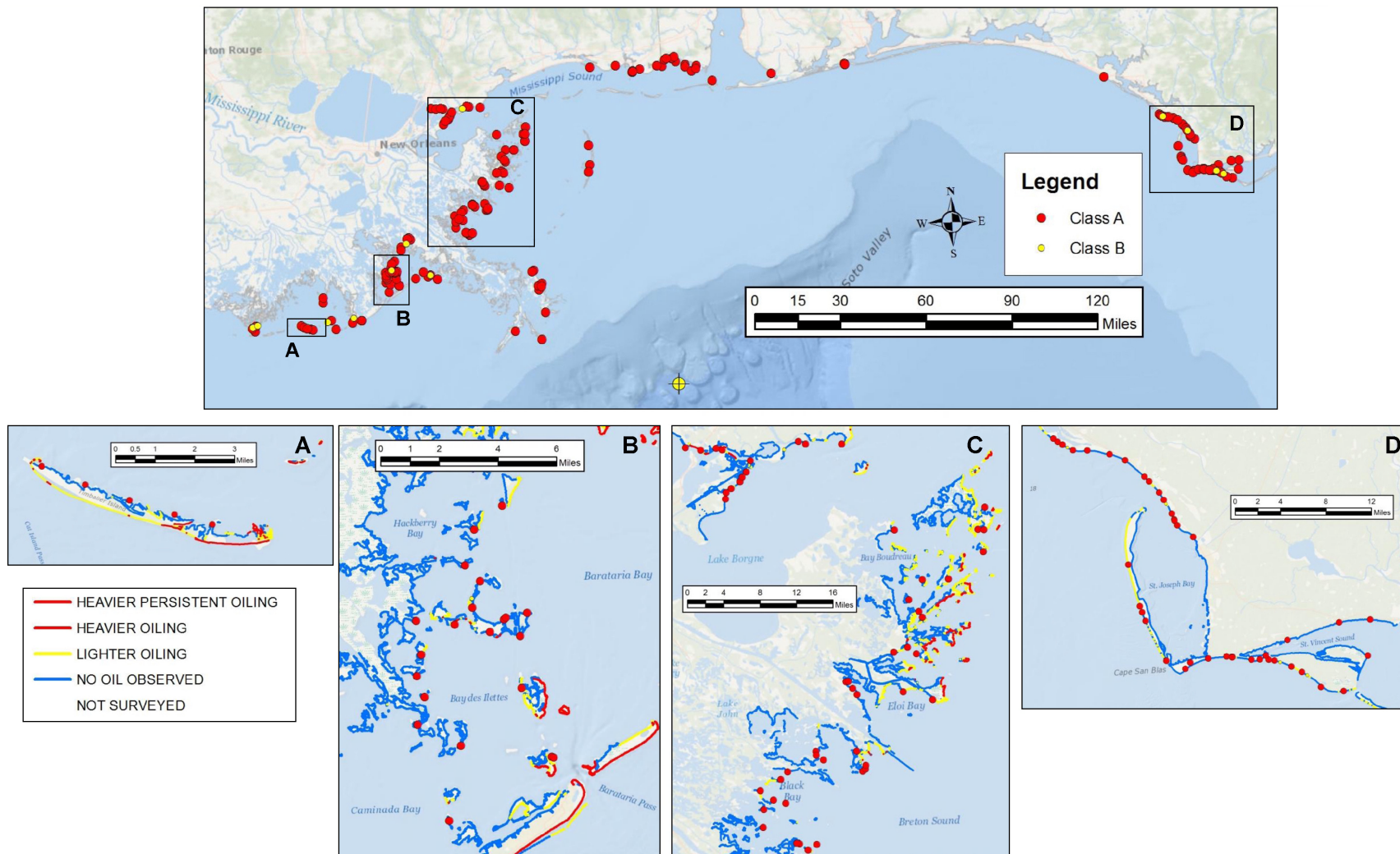


Figure 5: Maps showing the spatial extent of stranded Macondo oils from 2010 collected from supratidal and intertidal zones of shorelines indicated to have a maximum oil category of “no observed oil” during the SCAT program assessments. (A) Timbalier Island, (B) western Barataria Bay area, (C) Eastern delta and Lake Borgne areas, and (D) Apalachicola Bay area.

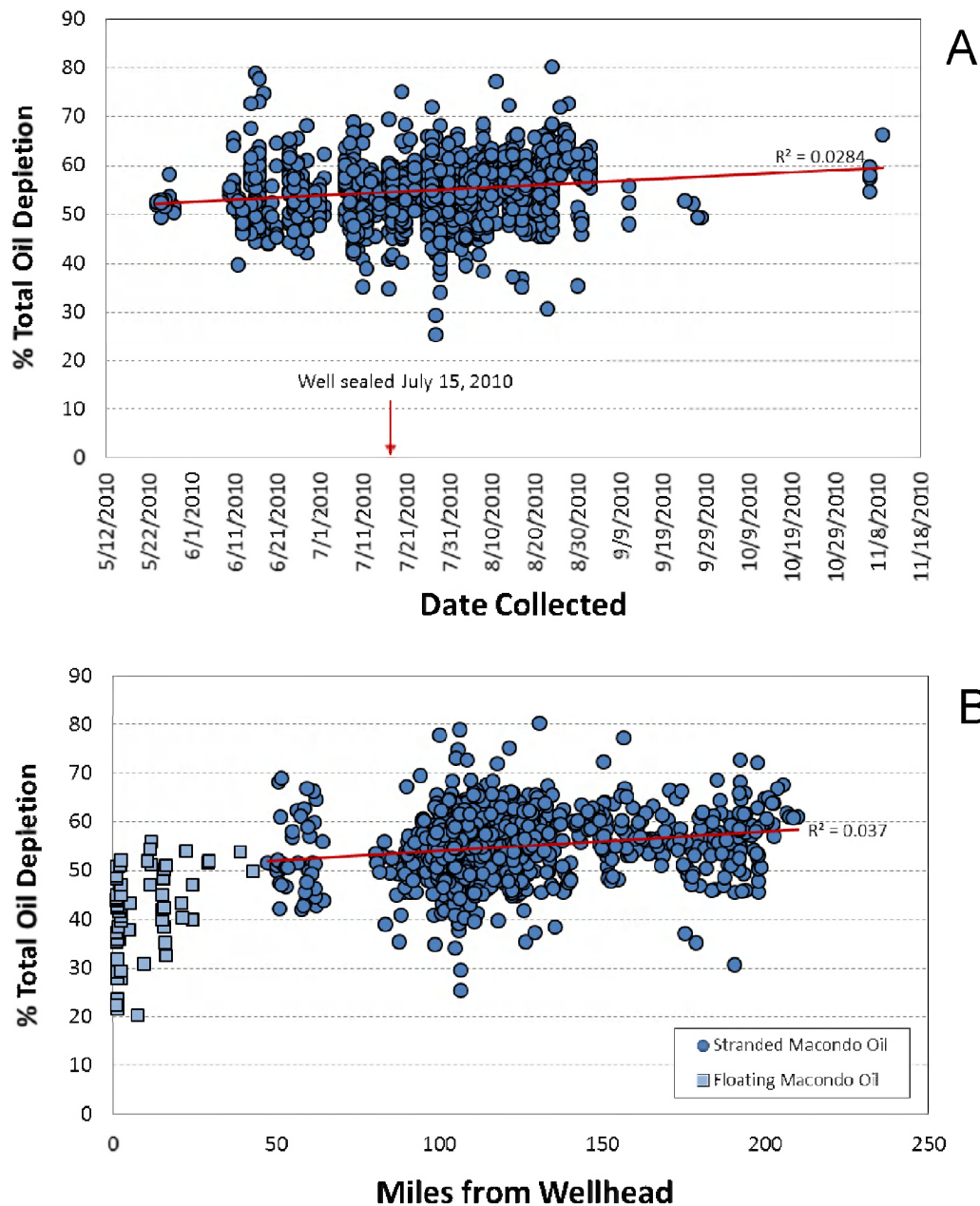


Figure 6: Plot of the %total oil depletion (weathering) in 1188 stranded Macondo oils versus (A) the date of collection and (B) distance from the Macondo well. Previously-studied floating Macondo oils are included in (B). Red lines in both depict linear best-fit with R^2 values given).

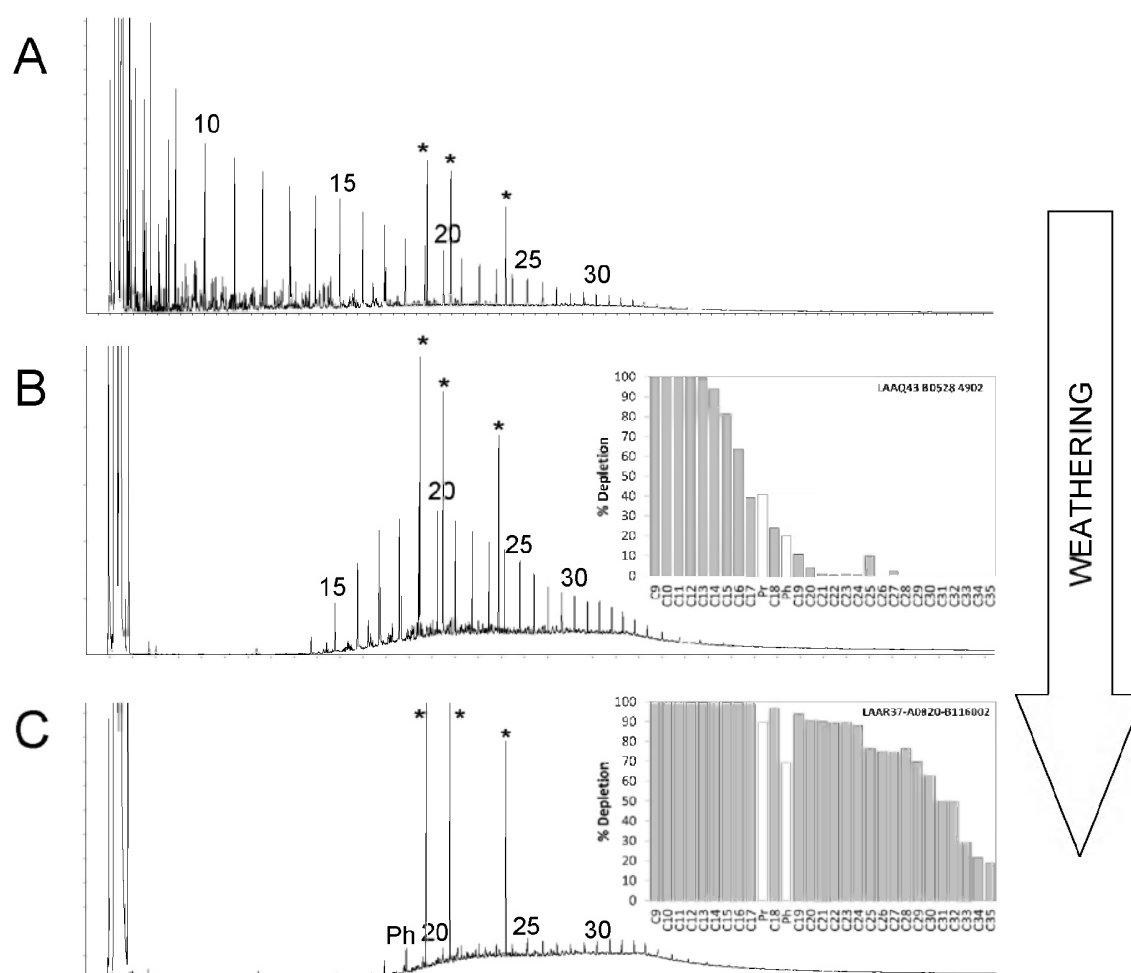


Figure 7: GC/FID chromatograms exemplifying the range of weathering among stranded Macondo oils. (A) fresh Macondo oil (GU2988-A0521-O9805; 1005074-03), (B) a minimally weathered stranded oil (LAAQ43-B0528-BA4902; 1209049-06), and (C) severely weathered stranded oil (LAAR37-A0820-B116002; 1008280-02). # - n-alkane carbon number; * - internal standard. Insets show %depletion of n-alkanes, pristane, and phytane per Eq. 2.

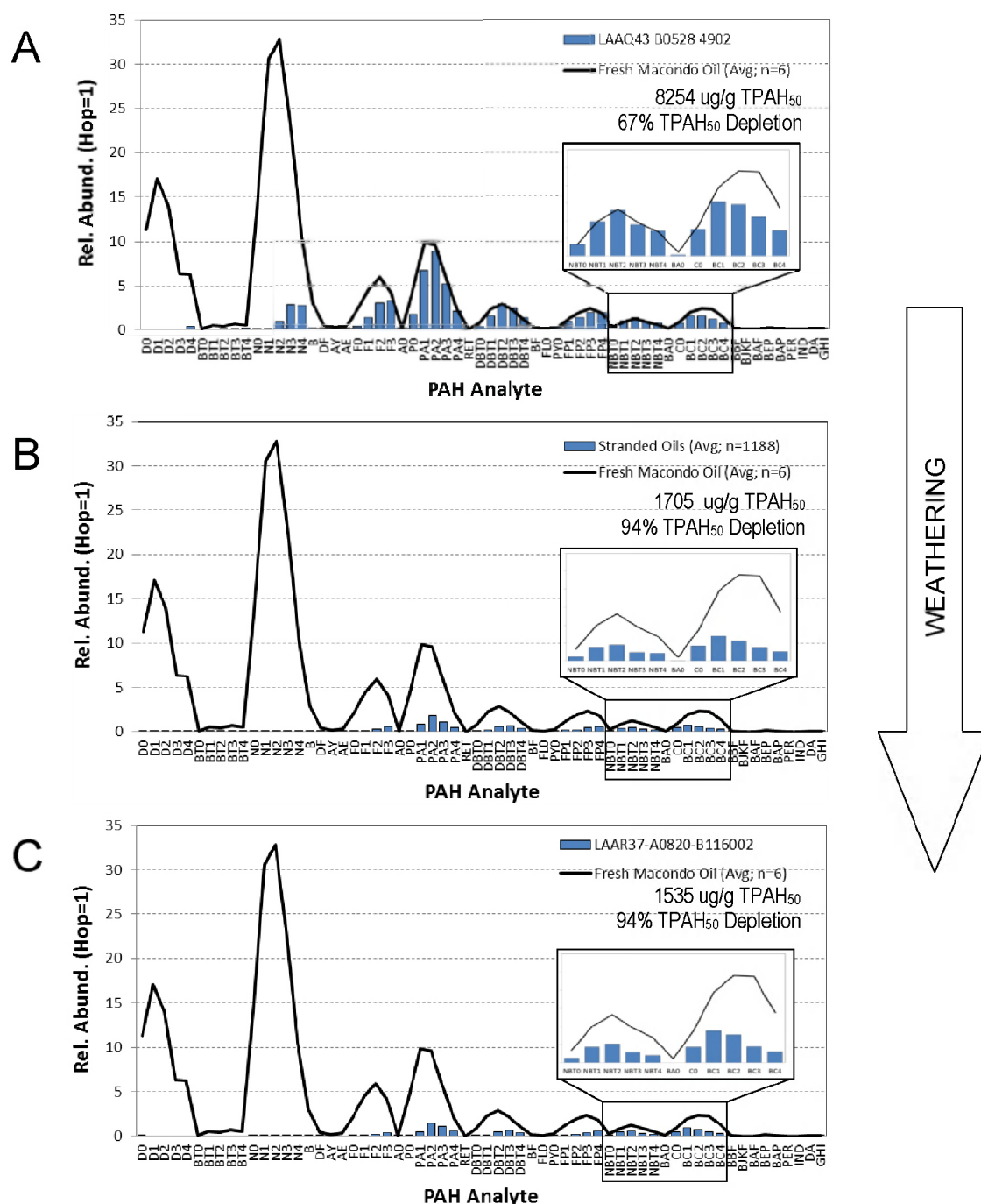
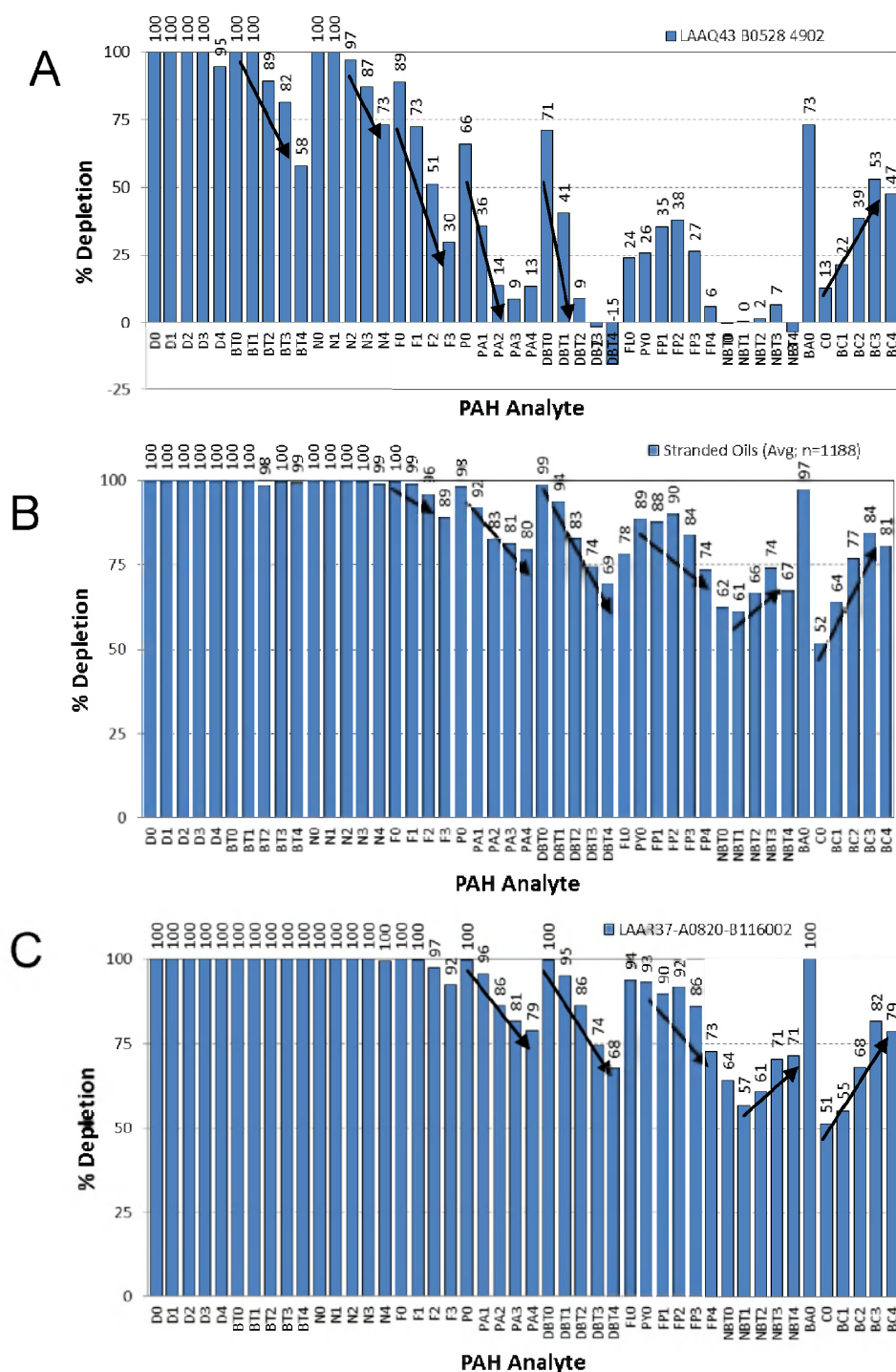


Figure 8: Representative hopane-normalized PAH histograms for variously weathered stranded Macondo oils from 2010. (A) a minimally weathered stranded oil, (B) average of all stranded oils, and (C) a severely weathered stranded oil. %TPAH₅₀ (N0-GH1) depletion calculated as per Eq. (2). Compound abbreviations from Table 2.



WEATHERING

Figure 9: Percent depletions of individual PAHs for variously weathered stranded Macondo oils from 2010. (A) a minimally weathered stranded oil, (B) average of all stranded oils (n=1188), and (C) a severely weathered stranded oil. %Depletions relative to hopane in fresh Macondo oil are calculated as per Eq. (2). Compound abbreviations from Table 2. Arrows depict trends in homologue groups.

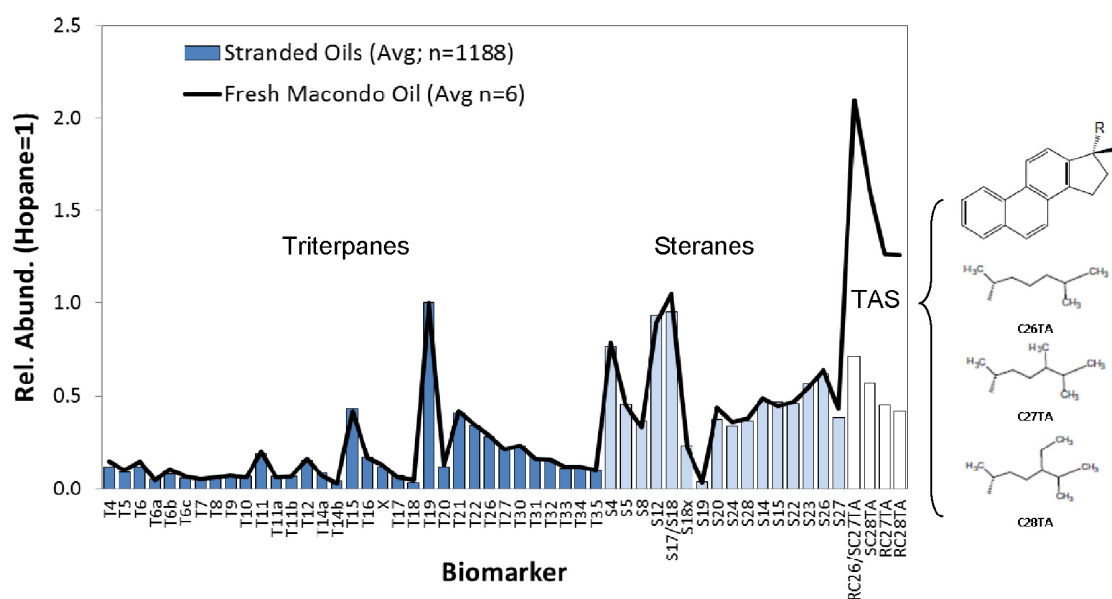


Figure 10: Hopane-normalized distribution of triterpanes, steranes, and triaromatic steroids (TAS) in average fresh and stranded Macondo oil. TAS are reduced in stranded oil due to photo-oxidation. Compound abbreviations from NDRA AQAP.